

CLAIMS

What is claimed:

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Art*
1. A process for the preparation of a supported metallocene catalyst comprising:

(a) providing a particulate catalyst support material comprising support particles having an alumoxane co-catalyst incorporated on said support particles;

5 (b) providing a dispersion of a metallocene catalyst in an aromatic hydrocarbon solvent;

(c) mixing said metallocene solvent dispersion and said alumoxane-containing support at a temperature of about 10°C or less for a period sufficient to enable said metallocene to become reactively supported on said alumoxane support material;

10 (d) recovering said supported catalyst from said aromatic solvent;

15 (e) washing said supported catalyst with a paraffinic hydrocarbon solvent at a temperature of about 10°C or less; and

(f) dispersing said washed catalyst in a viscous mineral oil having a viscosity greater than the viscosity of said paraffinic hydrocarbon solvent.

2. The process of claim 1 wherein the washed catalyst at the time of dispersion in said viscous mineral oil contains a residual amount of said paraffinic hydrocarbon solvent.
3. The process of claim 2 wherein the washing of said supported catalyst with said paraffinic hydrocarbon solvent is effective to reduce the residual aromatic solvent on said supported catalyst to a value of no more than 50 wt.% of said supported catalyst.
4. The process of claim 1 wherein said viscous mineral oil has a viscosity of at least 10 centistokes.
5. The method of claim 4 wherein said paraffinic hydrocarbon solvent has a viscosity of no more than 2 centistokes.
6. The process of claim 1 wherein subsequent to step (d) and prior to step (e) washing the recovered supported metallocene catalyst with an aromatic solvent to remove unsupported metallocene from said supported metallocene catalyst and thereafter washing said supported catalyst in accordance with step (e).
7. The process of claim 1 wherein said support material comprises silica-alumoxane particles having an average particle size within the range of 10-50 microns.

8. The process of claim 7 wherein said metallocene catalyst is a stereospecific metallocene incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, and both of said cyclopentadienyl groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures.

9. The process of claim 8 wherein said stereospecific metallocene is a syndiospecific metallocene characterized by the formula:

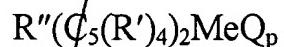


wherein Cp_a is a substituted cyclopentadienyl ring, Cp_b is an unsubstituted or substituted cyclopentadienyl ring; each R is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R'_m is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the cyclopentadienyl rings imparting stereorigidity to the metallocene and is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; $0 \leq p \leq 3$; $0 \leq m \leq 4$; $1 \leq n \leq 4$; and wherein R'_m is selected such that $(Cp_bR'_m)$ is a sterically different ring than (Cp_aR_n) .

10. The process of claim 9 wherein R is selected such that (Cp_aR_n) forms a substituted or unsubstituted fluorenyl group.
11. The process of claim 10 wherein Me is titanium, zirconium, hafnium, or vanadium.
12. The process of claim 11 wherein R'' is a methylene, ethylene, organosilyl, substituted methylene, or substituted ethylene radical.
13. The process of claim 12 wherein R is selected such that (Cp_aR_n) forms a substituted or unsubstituted fluorenyl radical having bilateral symmetry and R' is selected such that $(Cp_bR'm)$ forms an alkyl substituted or unsubstituted cyclopentadienyl radical having bilateral symmetry.
14. The process of claim 13 wherein the weight ratio of said alumoxane to said silica is within the range of about 0.5-1.5.
15. The process of claim 14 wherein R'' $(Cp_aR_n)(Cp_bR'm)$ forms an isopropylidene (cyclopentadienyl-1-2,7-di-tert-butyl fluorenyl) ligand or a diphenyl methylene(cyclopentadienyl-1-fluorenyl) ligand.
16. The process of claim 1 wherein said catalyst support material comprises particulate silica having a spheroidal configuration incorporating alumoxane co-catalyst and an average particle size within the range of 10-60 microns.

17. The process of claim 16 wherein said alumoxane co-catalyst is incorporated onto said silica particles predominantly on the surface thereof.

18. The process of claim 8 wherein said stereospecific metallocene is an isospecific stereorigid metallocene characterized by the formula:



wherein each $(C_5(R')_4)$ is a substituted cyclopentadienyl ring; each R' is the same or different and is a hydrogen or hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two $(C_5(R')_4)$ rings imparting stereorigidity to said metallocene with the two $(C_5(R')_4)$ rings being in a racemic configuration relative to Me ; and R'' is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal as designated in the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$.

19. The method of claim 18 wherein Me is titanium, zirconium, hafnium, or vanadium.

20. The method of claim 19 wherein R'' is a methylene, ethylene, organosilyl, substituted methylene, or substituted ethylene radical.

21. The process of claim 18 wherein the weight ratio of said alumoxane to said particulate silica support is within the range of about 0.5-1.5.

22. The method of claim 18 wherein said $(C_5(R')_4)$ groups are indenyl groups which are substituted or unsubstituted.

23. The method of claim 22 wherein said indenyl groups are each substituted at the proximal position.

24. The method of claim 23 wherein said isospecific metallocene is selected from the group consisting of racemic dimethylsilyl(2-methyl-4-phenyl indenyl)₂ zirconium dichloride, racemic dimethylsilyl(2-methyl indenyl)₂ zirconium dichloride, and racemic dimethylsilyl(2-methyl-4,5-benzo indenyl)₂ zirconium dichloride and mixtures thereof.

25. A process for the preparation of a supported metallocene catalyst comprising:

- (a) providing a particulate catalyst support material;
 - (b) contacting said particulate support material with an alumoxane co-catalyst carrier liquid;
 - (c) heating said mixture of support, carrier liquid, and alumoxane co-catalyst and temperature for a period sufficient to fix said alumoxane on said particulate
 - (d) cooling said mixture and separating said alumoxane-containing support from said carrier liquid;
 - (e) washing said alumoxane containing support material with an aromatic solvent to remove excess alumoxane therefrom;
 - (f) cooling said alumoxane containing support material to a reduced temperature of about 10°C or less and at said reduced temperature adding a dispersion of a metallocene in an aromatic solvent to said support material;
 - (g) mixing said metallocene, aromatic solvent, and support material at a temperature of about 10°C or less for a period of time to allow said metallocene to be supported on said support material with said alumoxane to provide a supported catalyst;
 - (h) recovering the resulting supported metallocene catalyst from said aromatic solvent;
 - (i) washing said supported catalyst with a paraffinic hydrocarbon solvent at a temperature of about 10°C or less; and

(j) thereafter dispersing said supported metallocene in a viscous mineral oil
25 having a viscosity substantially greater than the viscosity of said paraffinic hydrocarbon solvent.

26. The process of claim 25 wherein subsequent to step (h) and prior to step (i) washing the recovered supported metallocene catalyst with an aromatic solvent to remove unsupported metallocene from said supported metallocene catalyst and thereafter washing said supported catalyst in accordance with step (i).

27. The process of claim 25 wherein said metallocene catalyst is a stereospecific metallocene incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, and both of said cyclopentadienyl groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures.

28. The process of claim 25 wherein said catalyst support material in step (a) is particulate silica having a spheroidal configuration and an average particle size within the range of 10-15 microns.

29. The process of claim 28 wherein the particle size of said spheroidal particulate silica is increased by a value of at least .5 microns after the addition of said alumoxane on said support material.

30. The process of claim 25 wherein said alumoxane co-catalyst is incorporated onto said silica particles predominantly on the surface thereof.

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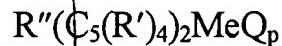
31. The process of claim 25 wherein said stereospecific metallocene is a syndiospecific metallocene characterized by the formula:



wherein Cp_a is a substituted cyclopentadienyl ring, Cp_b is an unsubstituted or substituted cyclopentadienyl ring; each R is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R'_m is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the cyclopentadienyl rings imparting stereorrigidity to the metallocene and is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; $0 \leq p \leq 3$; $0 \leq m \leq 4$; $1 \leq n \leq 4$; and wherein R'_m is selected such that $(Cp_bR'_m)$ is a sterically different ring than (Cp_aR_n) .
The process of claim 31 wherein the weight ratio of said alumoxane to said silica is within the range of about 0.7-1.0.

32. The process of claim 29 wherein the weight ratio of said alumoxane to said silica is within the range of about 0.7-1.0.

33. The method of claim 27 wherein said stereospecific metallocene is an isospecific stereorigid metallocene characterized by the formula:



wherein each $(C_5(R')_4)$ is a substituted cyclopentadienyl ring; each R' is the same or different and is

5 a hydrogen or hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two $(C_5(R')_4)$ rings imparting stereorigidity to said metallocene with the two $(C_5(R')_4)$ rings being in a racemic configuration relative to Me, and R'' is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal as designated in the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$.

34. The process of claim 33 wherein the weight ratio of said alumoxane to said particulate silica support is within the range of about 0.7-1.0.